

PHOENIX PHYSICAL LABORATORY CONTRIBUTIONS, No. 11.

THE SELECTIVE REFLECTION OF SALTS
OF CARBONIC AND OTHER
OXYGEN ACIDS

BY
LEIGHTON B. MORSE

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY
OF PURE SCIENCE, COLUMBIA UNIVERSITY

1907

Reprinted from
THE ASTROPHYSICAL JOURNAL, Vol. XXVI, No. 4
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I. THE SELECTIVE REFLECTION OF CARBONATES AS A FUNCTION OF THE ATOMIC WEIGHT OF THE BASE

If there were a regular displacement of the resonance periods of simple molecules in salts having the same acid radical, it should first be sought in compounds of simple bases having the same valence. The carbonates seemed especially well adapted to such a study since a large number could be obtained in a suitable form as minerals. The absence of water of crystallization adds further to the simplicity of the molecular structure of the carbonates of the eight elements (*Mg, Ca, Mn, Fe, Zn, Sr, Ba, and Pb*) examined, for which RCO_3 may be written as a general formula, *R* being a bivalent metal.

Partial data were obtainable on the reflection of the carbonates of two elements, calcium and magnesium. E. Aschkinass,² in a study of anomalous dispersion, had recorded the reflection of calcite and marble. He found maxima in the reflection of calcite at $6.67\ \mu$ and $11.40\ \mu$, and of marble at $6.69\ \mu$ and $11.41\ \mu$. By the method of "Reststrahlen" as discovered by H. Rubens and E. F. Nichols,³ J. T. Porter⁴ found a maximum in the reflection of white marble at $6.77\ \mu$.

Some time later W. W. Coblentz⁵ gave the reflection of calcite from $4\ \mu$ to $11\ \mu$, and of magnesite from $4\ \mu$ to $12.4\ \mu$, missing a second band in magnesite and not continuing to the second band in calcite, or to the region of the third bands in either. In the work of Aschkinass, Coblentz, and the present writer the wave-length determinations were referred to the dispersion of a rock-salt prism.

¹ *Phoenix Physical Laboratory Contributions*, No. 11.

² *Annalen der Physik*, 1, 60, 1900.

³ *Ibid.*, 60, 418, 428, 1897.

⁴ *Astrophysical Journal*, 22, 229, 1905.

⁵ *Investigations of Infra-red Spectra*, Parts III and IV, 81, 1906.

ARRANGEMENT OF APPARATUS AND ADJUSTMENTS

When the shutter at K was raised the image of a Nernst glower at N (Fig. 1)¹ was focused by the silvered concave mirror M_1 upon the surface under examination at S . A second silvered concave mirror M_2 caught the reflected beam and formed a secondary image of the source on the collimator slit C . These mirrors, M_1 and M_2 , were adjusted near each other in order to make the angle of incidence on the surface at S as small as possible.

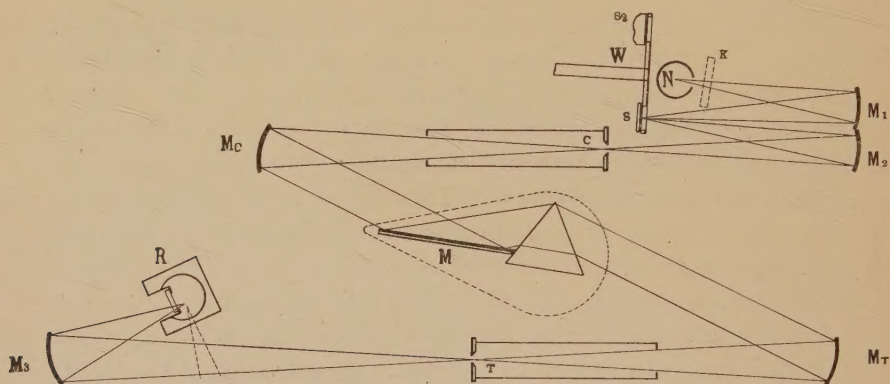


FIG. 1

After resolution by the spectrometer, the section of the spectrum passing through the rear slit T was focused on one of the radiometer vanes by a similar silvered concave mirror M_3 . The mirrors M_1 and M_2 were adjustable about horizontal and vertical axes perpendicular to the axes of the mirrors. A base provided with leveling screws aided in the adjustment of the mirror M_3 .

A small angle of incidence on the surface whose reflection was to be measured, 5° to 6° , was one of the advantages of this arrangement. Also the ability to use plane surfaces of small dimensions, but a little larger than the Nernst glower, made it less difficult to obtain suitable specimens.

Source.—A Nernst glower, operated on alternating current from the city lighting circuit was first used, but irregular fluctuations of

¹ The writer wishes to thank Mr. C. C. Chapin of the department, for valuable assistance given in preparing the curves and for drawing the figure.

the voltage produced not only sudden changes in the intensity of the radiation, but the expansion and contraction of the end wires continually shifted the image of the glower on the slit. Later a direct current glower (0.8 ampere, 110 volts) was used in a 120-volt storage-battery circuit, and slow variations in the current could be compensated for by a variable resistance, with the aid of an ammeter in circuit, reading to hundredths of an ampere.

After making these changes and improving the asbestos chimney used to protect the glower from variable air currents, conditions were so constant that no difficulty was experienced in holding the image of the glower on the spectrometer slit, *C*, for hours with no apparent shift in its position, and the emission of the glower remained equally constant. But for its selective emission, the Nernst glower used in this way would have been an ideal source.

Mounting of the specimens.—Three of the plane-polished mineral surfaces for which the reflection was to be measured, and a polished plane silver mirror were mounted over the four holes 2 cm in diameter in a wheel *W* (Fig. 1). The back face of the disk against which the surfaces were laid was ground as plane as possible on plate glass. But the final adjustment of the surfaces, to bring them successively into the same position when the wheel was rotated from one position to the next, was made by observing the reflected image of an incandescent-lamp filament in the field of a telescope with cross hairs. The smaller surfaces were mounted in cork and then adjusted on the wheel.

Spectrometer.—A Schmidt and Haensch reflection spectrometer with mirrors of 4 cm aperture and 35 cm focal length was used. By the aid of the Wadsworth¹ mirror-prism arrangement, the spectrometer arms remained fixed; and adjustment for the minimum deviation of one wave-length held for all. The face of the rock-salt prism was 5 cm by 8 cm and its refracting angle $59^{\circ} 59' 15''$. A rotation of the spectrometer arm by $4' 50''$ moved the center of the slit 1 mm. As the front and rear slits were always of equal width, the purity of the spectrum at any setting was as great as the energy necessary for a sufficient radiometer deflection would allow.

Wave-lengths were calculated from the indices of refraction for

¹ F. L. O. Wadsworth, *Phil. Mag.*, 38, 337, 1894.

rock salt given by H. Rubens¹ to $8.67\ \mu$ and the corrected values of H. Rubens and A. Trowbridge² were used for longer waves. Rotating the prism-table carrying the Wadsworth mirror-prism arrangement 1', corresponded to a change in wave-length from $6.50\ \mu$ to $6.60\ \mu$, from $11.60\ \mu$ to $11.65\ \mu$, or from $14.20\ \mu$ to $14.24\ \mu$, respectively.

As the spectrometer was arranged with its arms parallel and close to the prism-table, it was impossible to use any circular hood to protect the salt prism from moisture when it was not in use. In order that greater care might be taken to avoid touching the prism-table when removing and replacing the box used for this purpose, its top was made of glass. The plane sides and semi-cylindrical end of copper, outlined by dotted line in Fig. 1, left a space of 1 cm between the box and the pointed glass prism-table. A brass plate was mounted below the prism-table on a heavy collar about the spectrometer axis. The lower edge of the box fitted into a trough about the outer edge of this plate. Glycerine was used in the trough as a seal and P_2O_5 served as a drying agent.

Radiometer.—Behind the mirror M_3 was an inner brick wall to which the heavy shelf supporting the radiometer R and mirror M_3 (Fig. 1) was fastened. The radiometer was inclosed by a blackened compoboard box, not shown in the diagram. The Nichols' radiometer used was so similar to those described by other observers that only a few details of its construction are necessary. The mica vanes, $0.75\ \text{mm}$ by $5\ \text{mm}$, were mounted about $5\ \text{mm}$ apart and their front surfaces blackened with platinum black, held by shellac. The window of rock salt was protected by a P_2O_5 dryer when the radiometer was not in use. The half-period of the suspended system varied from twenty-five to fifty-five seconds, depending upon the air pressure in the radiometer. Often the general form of a reflection curve was obtained on one day and observations requiring the most sensitive conditions were made the following day, when the leak had increased the pressure, and with it the period and sensibility of the radiometer. The leak was so small that sufficiently accurate measurements have been made on the third day after the radiometer was pumped out, but the longer

¹ *Annalen der Physik*, 54, 482, 1895.

² *Ibid.*, 60, 733, 1897.

period made observing tedious. Generally the pressure used was such that the radiometer was slightly ballistic.

Because of the symmetry in the construction of the radiometer suspension, tremors of the building due to the heavy traffic outside at no time interfered with the progress of the work. Throughout the work no trouble arising from static charges on the radiometer vanes was encountered, not even when the stop-cock connecting the radiometer with the mercury pump was left open, a condition mentioned by Coblentz¹ as especially favorable for static disturbances. This was doubtless due to the presence of a small amount of radioactive material placed in the bottom of the radiometer case.

The image of an incandescent-lamp filament, projected on a scale one meter distant by a light concave mirror² attached to the lower end of the radiometer suspension, served to indicate deflections. An asbestos box covered the lamp used as an index and permitted light to pass from it only through a narrow slit on the side toward the radiometer. Diaphragms were used in addition to protect the radiometer from the heat of the lamp.

The walls of the room, an inner grating room, were light-tight with the exception of protected openings for ventilation. Unslaked lime was always kept in trays about the room to reduce the moisture in the air.

METHOD OF OBSERVING

A zero reading was taken before and after each deflection. Conditions were held so constant that the mean of two observations on the silver surface, one made before, and the other after observations on the three mineral surfaces, was sufficiently accurate for most of the work. There have been differences in these two deflections from silver which would have caused errors greater than those in reading the deflections from the mineral surfaces. Such occurrences were rare, even at points in the spectrum where the reflection from the mineral surfaces was high, and such observations were invariably repeated. But when the greatest accuracy in determining the posi-

¹ *Investigations of Infra-red Spectra*, Part I, Appendix III.

² To Dr. S. R. Williams the writer is much indebted for plating the mirror with platinum. The reflecting surface obtained remained in good condition throughout the work.

tion of a maximum was required, comparison was made between the mineral and silver surfaces at equi-distant points over the crown of the curve. These observations were then repeated with new settings on the same series of points in the spectrum and the maximum was determined from the average results.

When preliminary observations indicated little difference in the reflection maxima of two substances, as for example calcite and aragonite, both CaCO_3 , or siderite, and rhodochrosite ($\text{Fe}=55.5$, $\text{Mn}=54.6$), they were mounted in the wheel together with the silver mirror. This made it possible to determine the reflection of the two under almost identical conditions and slight errors in reading the spectrometer vernier were eliminated from the comparison. When the position found for a maximum seemed irregular, as for example the band of smithsonite in the third region, in addition to the usual frequent checking of the calibration curve of the spectrometer by setting on the sodium line, further assurance was sought by repeating observations with the substances in question and calcite in the "wheel" together.

DESCRIPTION AND ANALYSES OF SPECIMENS

Three of the mineral reflecting surfaces were polished by Schmidt and Haensch, witherite, strontianite, and aragonite. The others were polished in the laboratory. The polish required for such long waves was much less than for ordinary optical measurements. In fact the magnesite specimens containing silica were used when at normal incidence the image of an incandescent lamp one meter distant was barely visible in a reading-telescope. The range of quality of surfaces was from brilliant to very dull in the order given: witherite, strontianite, smithsonite, aragonite, calcite, rhodochrosite, siderite, cerussite, magnesite.

The writer is much indebted to Dean William Hallock for a number of useful suggestions concerning the preparation of the specimens and also for his friendly interest shown in many other ways.

To Professors Moses and Luquer and to Mr. Lamme, of the Department of Mineralogy, he is variously indebted for kindly advice in mineralogical matters and for the generous loan of materials from the departmental collection.

He is further indebted to Professor L. P. Gratacap, of the Museum

of Natural History, for the following description of the specimens used. The analyses were made by Dr. H. T. Beans, of the university.

1. Magnesite, No. 2, $MgCO_3$, from Oberdorf, Styria. Section from a mass, subcrystalline, fibrous, white; slight schillerization on surface from crystalline texture. Contained magnesium calculated as MgO , 15.94%; calcium calculated as CaO , 31.73%; Silica, 1.03%; water liberated at bright red heat, 0.48%.

2. Calcite, $CaCO_3$. Polished rhombohedral cleavage surface. Perfect texture, transparent.

3. Aragonite, $CaCO_3$. Section of transparent crystal. Surface used was a polished prism face.

4. Rhodochrosite, $MnCO_3$, from John Reed Mine, Lake Co., Col. Pale pink, semi-transparent, surface nearly parallel to face of rhombohedron.

5. Siderite, $FeCO_3$. Light brown, crystalline, lamellar. Contained iron calculated as FeO , 44.54%. Qualitative tests show some ferric iron and large quantities of manganese. No other qualitative tests were made.

6. Smithsonite, No. 1, $ZnCO_3$. Crystalline, dense texture, marked by lines of spheroidal intergrowth, pale yellow, to mottled in color, transparent, darkened by iron oxide nodule. Contained zinc calculated as ZnO , 60.58%; water liberated at bright red heat, 0.67%. The sample contains considerable iron.

7. Smithsonite, No. 2, $ZnCO_3$, from Laurium, Greece. Compact, fibrous, crystalline, pale milky gray in color, sub-transparent; original surface slightly mammilated. Contained zinc calculated at ZnO , 61.83%; water liberated at bright red heat, 0.59%.

8. Strontianite, $SrCO_3$. Massive, sub-fibrous, distinctly crystalline in structure, pale asparagus green.

9. Witherite, $BaCO_3$. Massive, fibrous, columnar in structure, pearl gray.

10. Cerussite, $PbCO_3$, from Monte Poni, Sardinia. Section obtained from twinned crystal, white, transparent.

RESULTS

Three bands of marked reflection¹ were found in all of the specimens examined (Figs. 2-7), but in no case were there more than three bands found in the spectrum between $4\ \mu$ and $15\ \mu$. The bands fall into three distinct regions in the spectrum grouped about $6.7\ \mu$, $11.5\ \mu$, and $14.5\ \mu$. To this grouping only one exception was found, magnesite, No. 1; and from the shape of its reflective curve the presence of a silicate was suspected. This was verified by a chemical analysis, which showed 8.95 per cent. of silica, calculated

¹ The reflection percentages given in the curves are based upon silver assumed total. The actual reflection of silver given by E. Hagen and H. Rubens (*Annalen der Physik*, 11, 73, 1903) increases from about 98 per cent. at $4\ \mu$ to 99 per cent. at $14\ \mu$.

as SiO_2 , together with 4.56 per cent. of water liberated at bright-red heat. Because of these impurities this specimen will not be considered further.

These regions where the carbonate reflection bands occur are distinct from the regions where the salts of other acids as far as known show reflection maxima. This verifies and gives a broader foundation for the conclusion reached by A. H. Pfund¹ based on a study of single bands in several nitrates and sulphates: "That the mechanism giving rise to these maxima was localized within the acid radical."

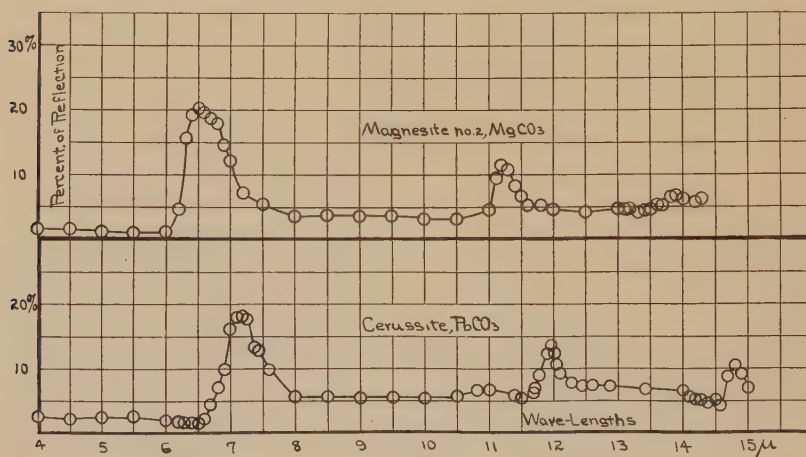


FIG. 2

In general the larger the atomic weight of the base the greater was the wave-length where the maximum reflection occurred, as will be seen by an examination of Figs. 2-7, of which Fig. 8 presents a condensed summary.

The following exceptions appear in the reflection curves found: siderite (FeCO_3) in the first region, either smithsonite (ZnCO_3) or siderite (FeCO_3) and rhodochrosite (MnCO_3) in the second region, and all three in the third region. Also, the reflection maxima of calcite and aragonite, both CaCO_3 , differ considerably in the second region both in magnitude and position; and the aragonite maximum may lie a little toward the long waves from calcite in the first region.

¹ *Astrophysical Journal*, 24, 23, 1906.

In attempting to answer the question: Can a law be found for the general shifting of the bands toward the long waves with the increase

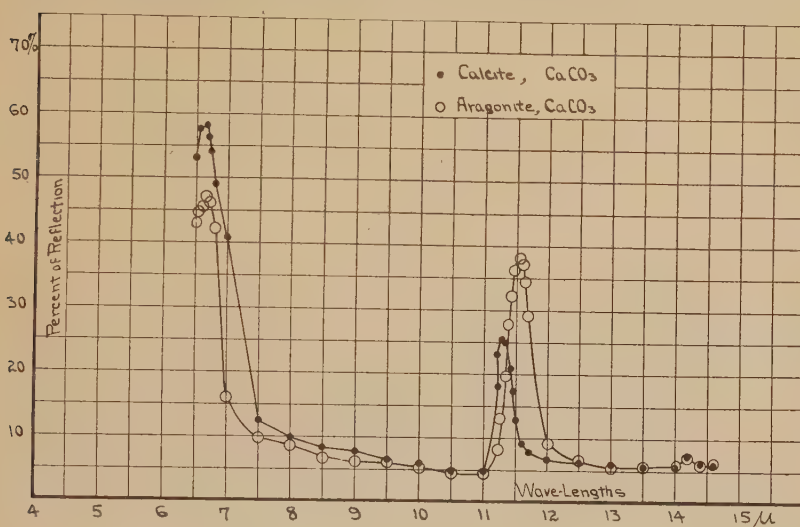


FIG. 3

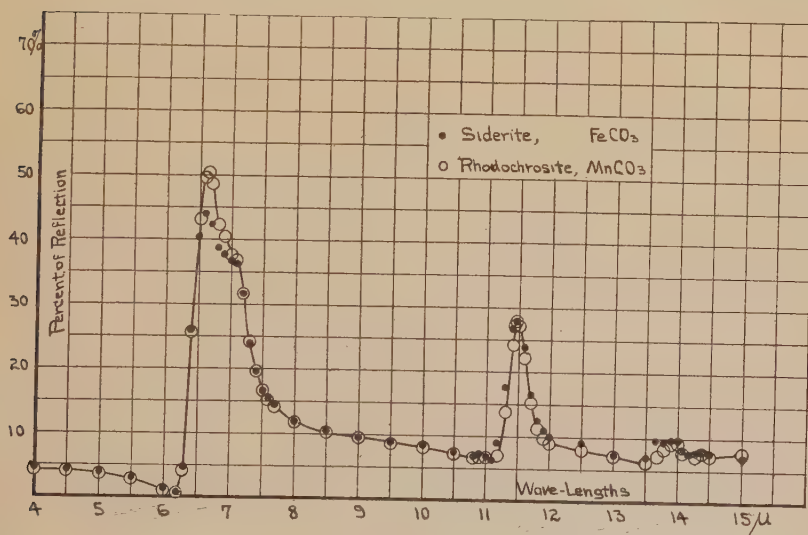


FIG. 4

in atomic weight of the base? a straight line was drawn in each region through the cerussite (PbCO_3) and calcite (CaCO_3) maxima. These

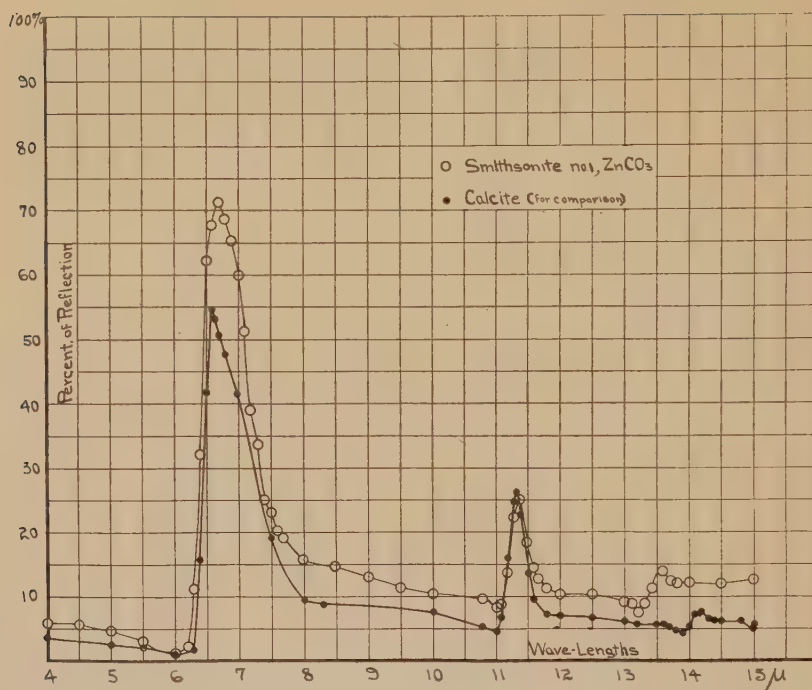


FIG. 5

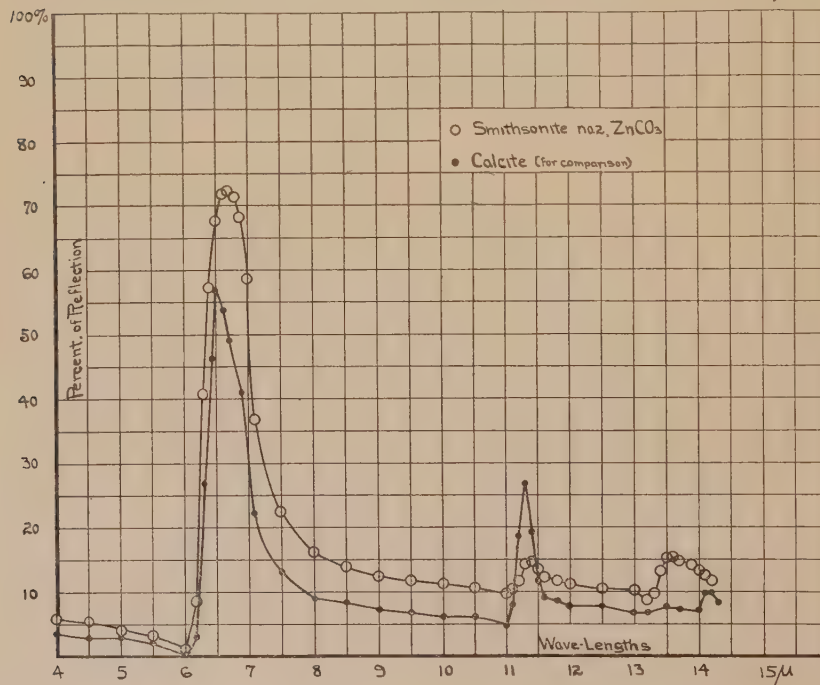


FIG. 6

points were selected to determine the lines C_1 , C_2 , C_3 , Fig. 8, because of the large difference in the atomic weight of the bases. Calcite rather than magnesite was selected as the lower point in determining the line because its structure gave evidence of its being the purer specimen.

Straight lines fitted the results better than any simple curve, showing that in general the shifts in position of the maxima are directly

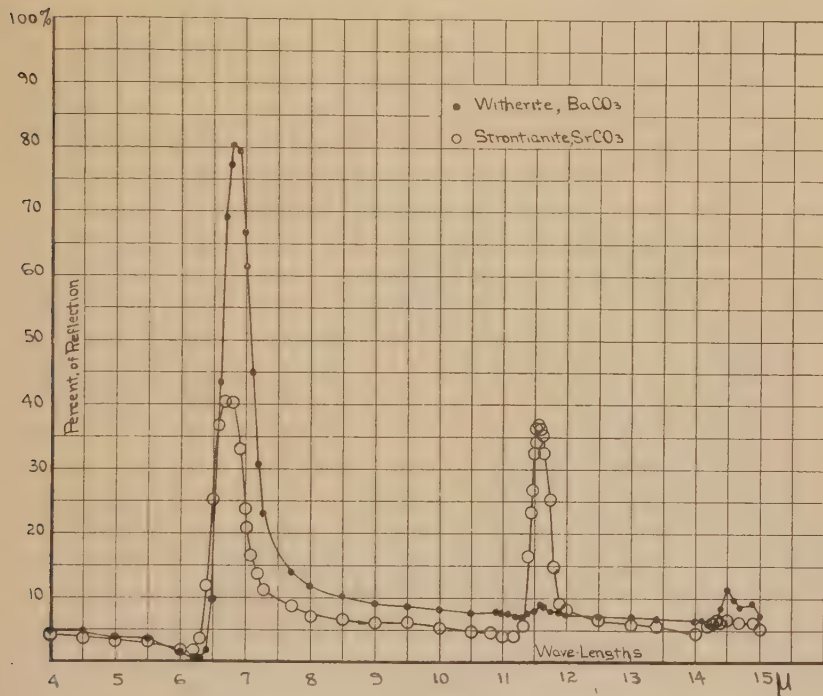


FIG. 7

proportional to the change in the atomic weight of the base. The smithsonite ($ZnCO_3$) band in the third region shows the greatest deviation.

A second specimen of smithsonite gave a band shaped differently, especially in the second region, but having practically the same maxima as the first in all three regions. Its band in the third region was several times as broad as the calcite band and had its maximum on the side toward the short waves. With the exception of the magnesite,

the other points showing the greatest deviation from the straight lines have been mentioned in the third preceding paragraph. These lines drawn through the cerussite and calcite (*Pb* and *Ca*) maxima, to aid in comparing the results, are practically parallel. All but three of the eighteen points in the first two regions lie near these parallel lines, which indicates that the average displacement in each region due to the same change in atomic weight of the base is of the same order of magnitude.

Half of the points in the third region are considerably off the line, but, as will be shown later, a larger allowance for errors must be made in this part of the spectrum. The reflection curves usually published where a rock-salt prism is used end before the beginning of these bands because of the rapid increase, with wave-length, in the absorption of rock salt in this part of the spectrum.

In the comparison of maxima it is well to recall that a band's position may be influenced by impurities in the specimen, by the selective emission of the source, or by the selective absorption of any medium in the path of the beam. A small per cent. of a salt with a strong reflection band near the true band of the carbonate might easily serve to broaden the band and shift its maximum, especially when the true band is of low intensity.

Errors.—In some respects the position of two of the three regions is rather unfortunate. In the first region the intensity of the emission of a Nernst glower varies¹ both rapidly and irregularly with change in wave-length, and water vapor has an absorption² band with a maximum at $6.1\ \mu$. In the third region the rapidly increasing absorption of the rock salt used as a prism and radiometer window would tend to displace the apparent position of maxima toward the short wave-lengths by an amount depending upon the form of the band. With slits 1 mm in width the reflection from silver at $14\ \mu$ was 119 divisions and but 47 divisions at $15\ \mu$. Some of the bands in this region were so low that it was possible to detect them only by repeating observations at short wave-length intervals, and when found it was difficult to determine the precise position of the maximum. The uncertainties besetting measurements here are further

¹ W. J. H. Moll, *Onderzoek van Ultra-roode Spectra*, Plate VIII, Utrecht, 1907.

² The total path of the beam in air was 2.7 meters.

increased by the wide slits¹ employed. The dispersion theory calls for a sudden drop just preceding a rise in reflection and, in nearly all cases, the curves show this in the third, as well as the two earlier bands.

Complexity of bands.—Irregularities in the shape of nearly all the bands in the first region, which were prominent when the points observed could all be plotted on a larger scale, are still quite distinct in the curves shown, especially in siderite and rhodochrosite. These irregularities, together with Coblenz's observation of two maxima in the first bands of calcite and magnesite suggest that a higher resolving power would show all the carbonate bands in the first region to be complex.

Few irregularities in the shape of bands were observed in the second region, but several appear in the third, though here the deflections were so small that it was difficult to distinguish between small errors in observation and true irregularities in the curve. The impurity of the spectrum resulting from the wide slits necessary in the study of the second and third bands may have not only depressed the maxima but concealed the details of any characteristic structure within the bands.

Structure, etc.—In general the data on record do not indicate that differences in the position of bands in substances with the same chemical composition should be expected so far out in the infra-red. But, if both aragonite and calcite, both calcium carbonate, are reasonably pure, as their structure would indicate, such a difference exists in the reflection from their crystals. The second bands differ considerably both in their position and in their magnitude. Moreover, the higher reflection of aragonite in the second region cannot be attributed to a surface difference, as calcite shows the higher reflection in the first.

No classification of the results according to the chemical group to which the base belongs has been possible. If displacements due to this are present they must either be irregular or secondary in magnitude to those produced by a change in the atomic weight. Neither has any simple relation been found to exist between the wave-lengths

¹ In the first, second, and third regions, slits 0.3 mm, 0.8 mm, and 0.1 mm in width were generally used.

of the regions within which the bands fall. For convenience of comparison the wave-lengths of the reflection maxima are given in Table I.

TABLE I

SUBSTANCE	CHEMICAL COMPOSITION	ATOMIC WEIGHT OF BASE	REFLECTION MAXIMA		
			Band 1	Band 2	Band 3
Magnesite.....	$MgCO_3$	24.2	6.5 μ	11.2 μ	13.9 μ
Calcite.....	$CaCO_3$	39.7	6.6	11.31	14.2
Aragonite.....	$CaCO_3$	39.7	6.65	11.55	14.2
Rhodochrosite.....	$MnCO_3$	54.6	6.63	11.47+	14.0-
Siderite.....	$FeCO_3$	55.5	6.60	11.47-	13.9-
Smithsonite.....	$ZnCO_3$	64.9	6.7	11.38	13.6
Strontianite.....	$SrCO_3$	86.9	6.76	11.56	14.37
Witherite.....	$BaCO_3$	136.4	6.86	11.60	14.5
Cerussite.....	$PbCO_3$	205.4	7.2	11.94	14.8

EARLIER DATA IN AGREEMENT

The earlier data on the reflection of the anhydrous salts of carbonic and other simple acids, though meager, are still in agreement with the conclusions drawn from carbonates concerning the shift of bands with change in the atomic weight of the base.

Carbonate.—In the data of Coblentz on calcite and magnesite the wave-lengths of both components of the complex band in the two substances lie in the order of the atomic weights of the bases. Although Coblentz gives the reflection of magnesite to 12.4 μ , his observations were at such long wave-length intervals that he missed the second reflection band which was doubtless present because the specimen used, judging from the height of the first band, was superior to the one here described.

Nitrate.—Pfund found that KNO_3 ($K=38.9$) and $AgNO_3$ ($Ag=107.1$) had bands at 7.05 μ and 7.45 μ respectively, shown by crosses in Fig. 8. Coblentz's value for KNO_3 , 7.15 μ , is shown by a circle.

TABLE II

Substance	Chemical Formula	Atomic Weight of Base	Maxima for First Band		
Anhydrite.....	$CaSO_4$	39.7		8.6 μ	9.1 μ
Celestite.....	$SrSO_4$	86.9	8.2 μ	8.76	9.1
Barite.....	$BaSO_4$	136.4	8.35	8.9	9.1

Sulphate.—The maxima in the reflection of simple anhydrous sulphates are given in Table II, compiled from the data of Coblenz.

In each case the maximum in the middle column is the highest and corresponds more closely to the center of the complex band. These values are plotted with the atomic weight of the base in Figure 8,

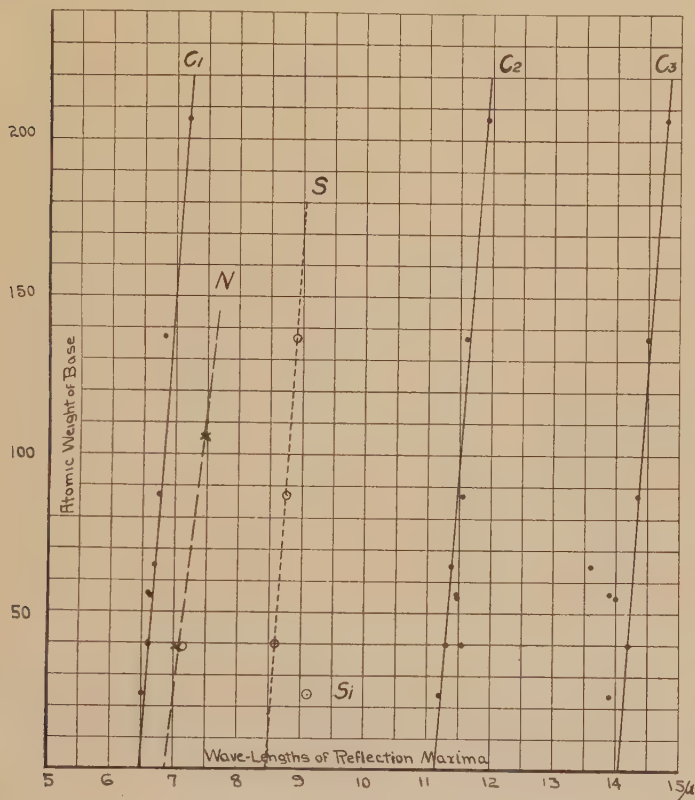


FIG. 8

and the line S drawn connecting these points is practically straight, showing that the displacements are proportional to the change in the atomic weight of the base, which agrees with the statement made regarding the displacement in carbonates. The line N , through the nitrate points, and the line S , through the sulphate points, are both approximately parallel to the lines, C_1 , C_2 , and C_3 , drawn for the three carbonate bands. From this we are led to suspect that the rate of

shift of the band with increase in the atomic weight of the base is of the same order of magnitude in carbonates, nitrates, and sulphates, though more complete data will be necessary to determine the exact relations and perhaps the significance of the different oxygen content of the acid radicals.

Silicate.—The circle¹ marked *Si* represents the position found for a band in enstatite ($MgSiO_3$).

II. THE RÔLE PLAYED BY OXYGEN IN THE SELECTIVE REFLECTION CHARACTERISTIC OF CARBONATES, NITRATES, SULPHATES, AND SILICATES

In this connection a somewhat broader phase of the subject presents itself, and we ask, Do the bands in these different acid radicals have any relation to each other?

The selective reflection of the salts (given in Table III) with bases having nearly the same molecular weight is compared. In Fig. 9 the weights of the elements combined in the acid radical with three molecules of oxygen are plotted as ordinates and as abscissae the wave-lengths of the first reflection bands. A straight line fits the results remarkably well, especially when one recalls that the lower atomic weight of magnesium is partly responsible for the highest point lying toward the short waves, and when one takes into account the difference in the values obtained by independent investigators for the KNO_3 band shown in the same figure (Fig. 9).

TABLE III

Substance	Chemical Composition	Atomic Weight of Base	Weight with 48 g of O	Position of Band
Calcite.....	$CaCO_3$	39.7	12g of C	6.6 μ
Potassium Nitrate.....	KNO_3	38.9	14 N	7.15* 7.05†
Anhydrite.....	$CaSO_4$	39.7	24 S	8.6 ¹
Enstatite.....	$MgSiO_3$	24.2	28 Si	9.1 ¹

* Coblentz, *loc. cit.*

† Pfund, *loc. cit.*

A change in the weight of the element combined with equal amounts of oxygen in the acid radical produces a much larger shift in the position of the reflection maximum than is produced by the same change

¹ Coblentz's data in Fig. 8 shown by circles, Pfund's by crosses.

in the atomic weight of the base. This is in agreement with the chemist's views regarding the relative strength of the bond existing in the two positions. Similar considerations suggest that peculiarities of the individual elements other than the differences in their atomic weights may be found to exert a stronger control when within the acid radical

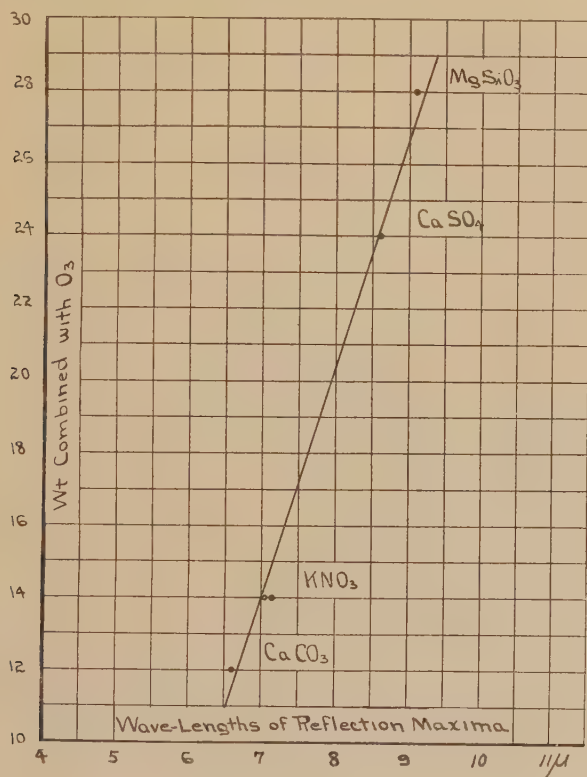


FIG. 9

than they do in the base, and similarity or dissimilarity of its relation to the oxygen in the acid radical must be carefully studied.

In this we may have a clue to a general method by means of which chemical formulae may come to have a more definite and wider dynamical meaning than they now do. At present, atomic relations within the molecules of a solid can only be inferred from evidence gained primarily from solutions and gases.

From the foregoing results it appears that there is a regular shift in the reflection bands, characteristic of a given acid radical, with a change in the atomic weight of the base with which it is combined; and second, that the active and characteristic element in the carbonic, sulphuric, nitric, and silicic acid radicals is oxygen. A change in the atomic weight of the element, combined *directly* with the *oxygen* in the acid radical, is far more potent in shifting the wave-length of the reflection band, than the same change in the atomic weight of the base, which is *indirectly* combined with the oxygen.

To establish the second hypothesis on as firm a footing as the first now rests, it may be necessary to give to salts of other acids the same systematic study which the carbonates have received, and in doing this the writer is at present engaged.

SUMMARY

1. The reflection curves for all the carbonates examined show between $4\ \mu$ and $15\ \mu$ three, and only three, bands of marked reflection.
2. The bands fall into three separate and definite spectral regions, which are distinct from the regions where the salts of other acids, so far as known, show reflection maxima.
3. With few exceptions, an increase in the atomic weight of the base causes a shift of all three reflection maxima toward long waves by an amount roughly proportional to the change in atomic weight of the base.
4. No regular displacements traceable to the chemical group to which the base belonged were observed, nor does any simple relation appear between the wave-lengths of the three bands in carbonates.
5. Combining with the data on carbonates the scattered observations on nitrates, sulphates, and silicates, the tentative hypothesis has been made that the oxygen atom is the one chiefly responsible for the marked reflection observed.
6. The results presented in the present paper suggest a new and far-reaching method by which it may some time be possible to express the dynamical relations existing between the separate atoms of a molecule, and thus the present conception of chemical bonds and linkages be given a broader significance.

In conclusion, the author wishes to thank Professor E. F. Nicho

who suggested the problem and directed the work, for the daily interest shown; but he would like especially to express his deep appreciation of the profit he has derived from frequent discussions during the progress of the work concerning its broader relations.

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August 1907

ADDENDUM

Since the foregoing paper went to the printer my attention has been called to a short paper in the *Jahrbuch der Radioaktivität und Elektronik* (4, 132, 1907) by Dr. W. W. Coblentz in which, after reporting the analysis of the first reflection band in eight carbonates and the reflection and absorption bands between 4μ and 9.4μ in seven sulphates, diagrams are given and the following conclusions drawn:

Im ganzen genommen reichen die dargestellten Ergebnisse hin, um nachzuweisen, dass das Molekulargewicht tatsächlich die Lage des Maximums beeinflusst; es ist aber zu beachten, dass die Verschiebung durch das metallische Atom oder "Ion" verursacht wird an welche die Atomgruppe gebunden ist. Andererseits wird, nach früheren Ergebnissen, die Lage des Maximums durch die Anzahl der Atomgruppen nicht beeinflusst. Dasselbe gilt auch für das Kohlenstoffatom an sich. Die Atomgruppen sind mithin als die Ursache gewisser charakteristischer Absorptions- und Reflektionsbanden zu betrachten; die Lage dieser Banden aber wird durch das Atomgewicht des metallischen Atoms bestimmt, mit dem vereinigt die Atomgruppe die Verbindung bildet.

Dr. Coblentz's paper is dated March 22, 1907. Before this, a considerable portion of the data here presented had been gathered.

L. B. M.

